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Stevens Inst. Tech., Hoboken, N.J.

First Semi-Annual Report ~~on~~ (NASA Contract NSG-494)
Grant

Dr. L. Z. Pollara, Principal Investigator
Dr. F. B. Clough, Co-Investigator

Title

A Quantitative Study of Solutions Through Gas Chromatography

15 Sep. 1963-

10 Mar. 1964

Report Prepared By

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I. Administration of the Contract

A. Personnel

Dr. Francis B. Clough, Associate Professor of Chemistry at Stevens, has agreed to collaborate with Dr. Pollara on this research program.

David C. Locke, who is now completing his Doctoral studies at Kansas State University, has been appointed Post-Doctoral Research Fellow under the provisions of the contract. He will assume his responsibilities in June, 1964.

Appointment of a Graduate Research Assistant under the provisions of the contract has been postponed to the academic year 1964-65, largely due to unavailability of a suitable candidate.

B. Activity to Date on the Research Project

Before the proposal was finally funded, much of the experimental work envisioned in the proposal was carried out by Daniel E. Martire, in the course of his Ph.D. research. The original hope was that Dr. Martire's final year of doctoral research would be supported by this contract, but it was necessary to find other ways to support him. The work was made possible through the use of the facilities of the Esso Research and Engineering Company. An account of Dr. Martire's work is included in this report.

This mistiming of the term of the contract with the schedule of studies for Dr. Martire slowed further progress on the research during the fall of 1963. Additional details are set forth in Stevens' letter to Dr. Smull dated 22 September 1963. A further complication has been the illness of the principal investigator, Dr. Luigi Pollara. It is expected that the collaboration of Dr. Clough will partially remedy this loss of time and prepare for the arrival of the Post-Doctoral Fellow in June 1964.

C. Projected Activity on the Research Project

Until June, Dr. Clough will cooperate with the Principal Investigator in following up the work begun by Dr. Martire. The establishment of laboratory facilities as indicated in the proposal will be included. In June Dr. Locke will join the group, and in September 1964 a pre-doctoral Graduate Research Assistant will also begin working on the project.

II. Results from the Investigation to Date

The results obtained thus far in this research project are described in the Doctoral Dissertation of Daniel E. Martire*. Although this work was not supported by the contract, it is the basis for further work under the contract, and will be described below. The abstract of the Dissertation is appended to this report.

* Daniel E. Martire, "An Investigation of the Thermodynamics of Dilute Non-Electrolyte Solutions by Means of Gas-Liquid Chromatography," Ph.D. Thesis, Stevens Institute of Technology, 1963. University Microfilm, Mic 63-6981, Ann Arbor, Michigan. Most of this work will appear in "Advances in Chromatography," Vol. I, edited by J. C. Giddings and R. A. Keller, shortly to be published by Marcel Dekker, Inc.

A. Validity of Activity Coefficients Determined by Gas-Liquid Chromatography

Martire analyzed the question of the validity of the activity coefficients deduced from gas chromatographic data. When the precautions he stressed are observed, activity coefficients for solutes at infinite dilution obtained by this method seem accurate to within 2% (and probably reproducible to within 1%).

The essential precautions are as follows: Sample sizes must be small, and the column packing should be at least 15% liquid to minimize the possibility of adsorption on the solid. Accurate measurement is required of column temperature, initial retention time, temperature of the flowmeter,

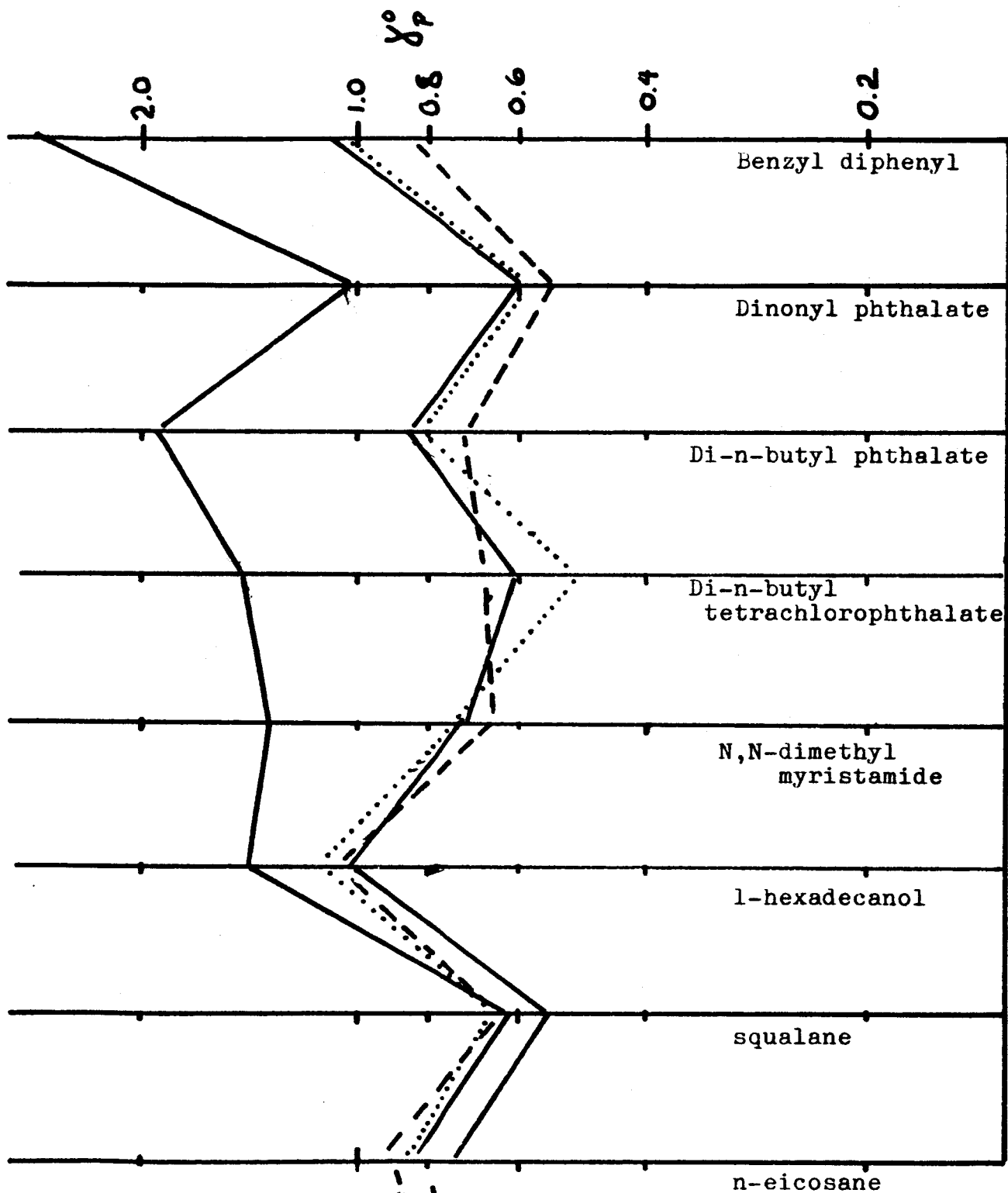
inlet and outlet pressures, flow rate, and weight of the liquid phase. After considering the observed variations of corrected retention volumes with flow rate, Martire recommends that average values of the specific initial retention volumes be taken for activity coefficient computations. His reason is that any justifiable extrapolation procedure would require an impractical extension of experimental time, with little improvement in accuracy.

The computation of the activity coefficients requires also a knowledge of the fugacities of the solute vapors at the vapor pressure of the solute. These fugacities are available for many hydrocarbons, but satisfactory values for polar solutes are not easily obtained. Since a comparison of solute behavior is a principal objective of this research, all of the activity coefficients in Martire's thesis were calculated using vapor pressures for fugacities. A finer correction involves interactions between the solute and the carrier gas. The experimental study of these corrections holds open the interesting possibility of obtaining second virial coefficients for the interactions of gases, from gas-liquid chromatography data.

B. Results of the Experiments

Since the main objective in this research is to analyze interactions between molecules in solution, the experimental work was designed to provide data under uniform conditions on a broad spectrum of solvent-solute pairs. Forty-four solutes, including aromatic and aliphatic hydrocarbons, and halogenated hydrocarbons were studied in eight different carrier liquids as solvents. The eight solvents, which had to be of low volatility, were n-eicosane, squalane, 1-hexadecanol, N,N-dimethyl myristamide, di-n-butyl tetrachlorophthalate, di-n-butyl phthalate, dinonyl phthalate, and benzyl diphenyl.

A sampling of the activity coefficients obtained from these experiments



ACTIVITY COEFFICIENTS AT
INFINITE DILUTION
[GLC DATA - 74.1°C]

Fig. 1

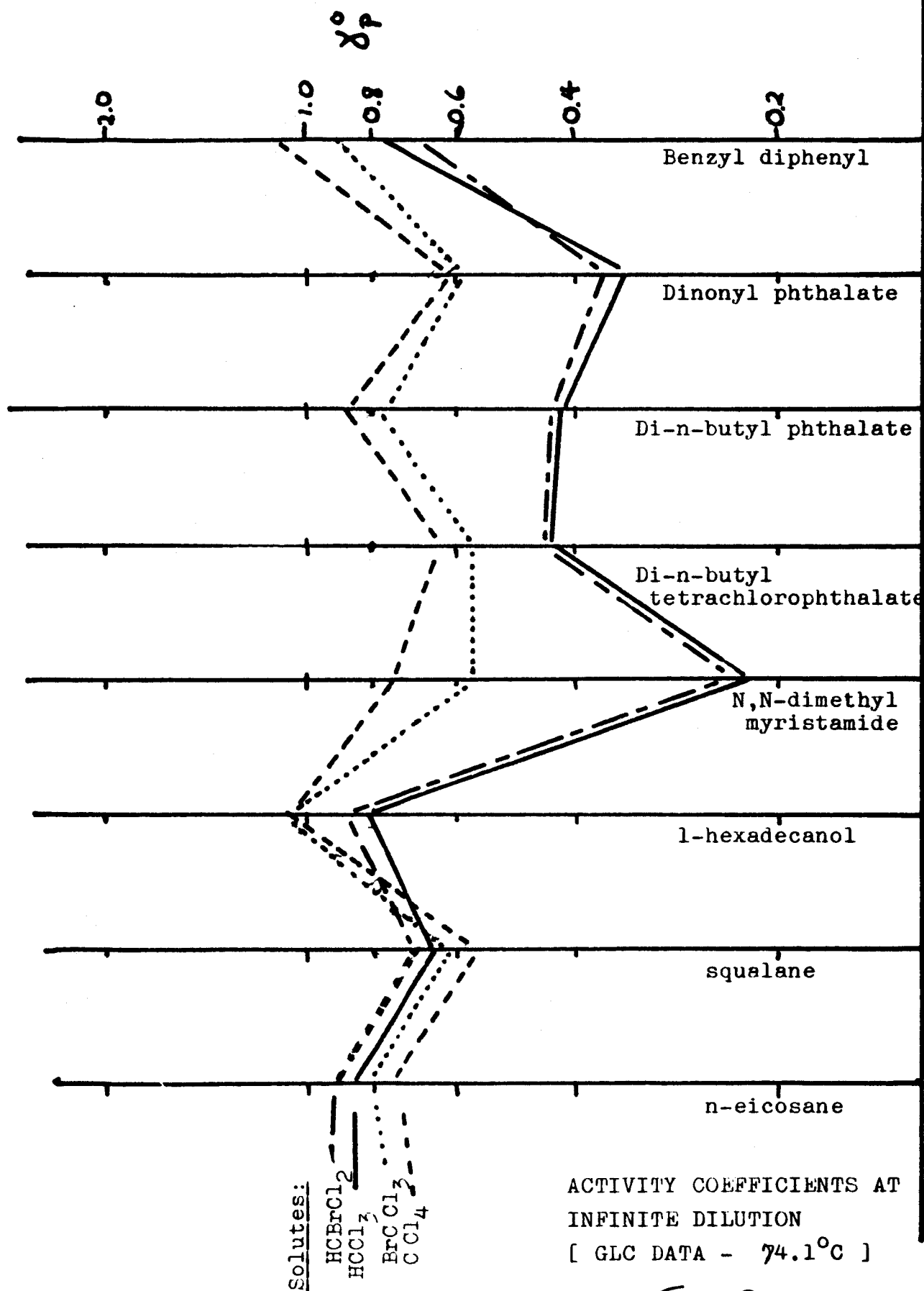


Fig. 2

(γ_p^o , calculated using solute vapor pressures in place of fugacities) are presented in Figs. 1 and 2. For other values and full details reference must be made to Martire's thesis. The results presented here will serve to indicate the possibilities of comparison which these data afford.

C. Interpretation of the Results

Reflection on these and other data in the light of contemporary theories of solutions brings sharply into focus some of the shortcomings of these theories, and leaves the impression that new tacks must be taken before an adequate theoretical understanding of activity coefficients can be obtained. Contemporary theory does, however, shed light on many aspects of solution behavior.

Within the concept of a regular solution, the activity coefficient can be thought of as the superposition of two parts: $\ln \gamma_2^o = \ln \gamma_2^s + \ln \gamma_2^e$. The first part, $\ln \gamma_2^s$, is regarded as a statistical contribution related to the difference in size of the two molecules; this contribution can be estimated, and the contribution will always yield negative deviations from Raoult's law. The second part, $\ln \gamma_2^e$, can be estimated, following the Hildebrand-Scatchard treatment, by the equation $\ln \gamma_2^e = \frac{v^*}{RT} (\delta_1 - \delta_2)^2$ where δ is the solubility parameter (the energy of vaporization per cm^3). These contributions will always be positive deviations from Raoult's law.

Martire made use of this relationship to discuss data of Desty and Swanton (1961) on aliphatic and unsaturated hydrocarbons in aromatic solvents. While the results of this treatment were gratifyingly good, the approximations involved show that this approach leaves much to be desired. One significant observation, however, is that the contribution from the size difference is clearly present in Martire's data. In particular, Martire showed that the difference in molecular size of squalane and eicosane, the two hydrocarbons used as solvents, could account for, in a reasonably quantitative way, the

differences in activity coefficients in these solvents. The parallel behavior of the activity coefficients in squalane and eicosane can be observed in the charts accompanying the previous section.

The technic of factor analysis, as described in the next section, holds promise of being of great help in developing new semi-empirical theories of solute-solvent interactions.

D. The Application of Factor Analysis to the Utilization of Activity Coefficient Data

Dr. Pollara and his students have had considerable success in applying the technic of factor analysis to correlation of various properties of substances. This technic has been used by Martire, to develop a way of examining the effectiveness of particular liquid substrates for GLC separations.

The essential problem that must be resolved, for this application, is how to interpret the variations observed in $\ln \gamma$ in terms of fundamental properties and interactions of molecules. Generally, one searches for a linear equation in the properties. To illustrate, suppose that the polarizability, α , and the molar volume, v , of the solvent were the only significant properties. Then, for solvents 1 and 2 and solute 1, equations as follows would be expected:

$$\ln \gamma_{11} = a_1 \alpha_1 + b_1 v_1$$

$$\ln \gamma_{21} = a_2 \alpha_1 + b_2 v_1, \text{ and so forth.}$$

The a_i and b_i are solute factors to match the solvent factors α_1 and v_1 . In another solvent, with factors α_2 and v_2 :

$$\ln \gamma_{12} = a_1 \alpha_2 + b_1 v_2$$

$$\ln \gamma_{22} = a_2 \alpha_2 + b_2 v_2, \text{ and so forth.}$$

In general, when more factors must be included, a_1 and b_1 are examples of solute factors n_{1j} , while α_2 and v_2 are examples of solvent factors q_{j2} . An equation for solute i in solvent k would then be written as

$$\ln \gamma_{ik} = \sum_j n_{ij} q_{jk}$$

summed over all the various terms j .

While analysis of data into equations of this sort is frequently attempted, two difficulties generally arise. It is seldom clear how many factors are needed, or even whether some factors included are redundant; and it is not easy to discover just what are the relevant factors. It is the first of these questions which is most specifically attacked by factor analysis--just how many factors will be sufficient. The second question, that of discovering the relevant factors in terms of measurable molecular properties, remains a task for chemical insight. Once, however, the hypothesis is made that certain factors cover the requirements, factor analysis again furnishes a technic for testing the hypothesis, and for generating the final coefficients, e.g., the n_{ij} .

In Martire's study, it did not seem possible as yet to isolate the physical parameters appropriate to the description of the activity coefficients (or $\ln \gamma$) for solutes in various solvents. This remains a desirable goal. However, chemical insight was used in choosing the solutes and solvents for the study, with the aim of "spanning the solute and solvent factor space," i.e. of including in the solvent-solute pairs all of the types of interactions necessary to cover the most general situation.

One set of data -- all of the activity coefficients in one solvent (dinonyl phthalate, DNP) and all of the coefficients for five solutes -- were set aside, to be used to check the results of the factor analysis. A factor analysis was then carried out, at each of the three temperatures of the study, on the values of $\ln \gamma_p^0$ for the remaining 39 solutes in seven solvents. The result of this treatment was the discovery that only five terms were needed (i.e., j runs from 1 to 5) in the equations $\ln \gamma_{ik} =$

$\sum n_{ij}q_{jk}$ to reproduce the data within experimental error (2%). The analysis yields values for the solute factors, n_{ij} , and solvent factors q_{jk} , but of course does not, as observed above, tell how they are to be interpreted in physical terms. Actually this analysis leaves us with 5×39 solute factors and 5×7 solvent factors, which then, if we were successful in choosing data to span the factor space, should make possible prediction of other data from only a few measurements.

The first test of this result was to apply it to the data which had been set aside. For the solvent DNP, the five factors, q_j , required were obtained by using $\ln \gamma$ values for five solutes in DNP expected to span the solute factor space. (Here chemical intuition!) These values were next used in conjunction with the solute factors n_{ij} to recompute the activity coefficients of the remaining 34 solutes in DNP, obtaining excellent agreement with the experimental values.

The next test was to take the data on the five solutes set aside, and determine the solute factors, n_{ij} , for each of them from the data in a suitable set of five solvents, the solvents this time being chosen to span the solvent space. These values could then be used to reproduce the $\ln \gamma$ values for the solutes in the remaining three solvents, with excellent to fair agreement with experiment.

The success of these tests establishes the practical value of the factor analysis. They illustrate, respectively, the procedure for characterizing a new solvent for gas-liquid chromatography, and the procedure for deciding what solvents would best separate a particular solute from a mixture. In either case five experimental determinations of activity coefficients (i.e., of specific retention volumes) are sufficient. The solvent or solute factors obtained from these could then be used to calculate relative volatilities

of solutes in proposed separations, thereby deciding the most effective conditions for a separation without the great expense of further experiment.

The only question detracting from a general application of this scheme is how well the study has covered the variety of solvent-solute interactions. This remains to be seen, but it seems probable from the evidence available that the technic of factor analysis with these data goes a long way towards providing a rapid, certain way of choosing the solvent to obtain highest efficiency in any given gas-liquid chromatography separation.

III. Research Planned for the Coming Year

The proposal for which this grant was awarded called for a study of 60 solutes in 20 solvents. Martire's work (performed at Esso Research and Engineering Company) covered 44 solutes in only 8 solvents. The success of his study, in particular the application of factor analysis, will make possible shortening the labor of studying the remaining combinations on the original list, and the insights obtained will suggest other solutes and solvents to focus attention on.

During the summer 1964, the laboratory at Stevens will be ready for use in collecting data. Systematic application of the technic of factor analysis to data collected to characterize the solutes and solvents will enable prediction of other activity coefficients. These will then be determined experimentally only as far as they give useful information.

The studies of the theory of solutions begun by Martire will be pushed. In particular, attention will be given to alternatives to the Hildebrand-Scatchard approach. The information already collected on temperature dependence of the activity coefficients has not yet been exploited.

A further aspect of the study of the fundamental theory of solution

interactions is the possibility of obtaining interaction virial coefficients from the data. We want to explore fully this interesting possibility.

Later an extension of the range of applications and new insights may be obtained through the study of selected inorganic compounds. Consideration will be given during the year to more imaginative extensions of the research. Mr. Locke, the Post-Doctoral appointee to join us in June, with a background in gas-liquid chromatography, has expressed interest in fused salt systems, and in low molecular weight solvents.

Appendix

The Abstract, "An Investigation of the Thermodynamics of Dilute Non-Electrolyte Solutions by Means of Gas-Liquid Chromatography," Daniel E. Martire, Ph.D. Dissertation, Stevens Institute of Technology, 1963.

It has been shown that the activity coefficient for the solute component at infinite dilution in the liquid phase can, in principle, be measured by means of gas-liquid chromatography (G.L.C.). However, to obtain thermodynamically sound and accurate values, certain experimental precautions must be taken and the resulting data must be critically analyzed. Accordingly, activity coefficients have been measured for forty-four solutes in eight solvents (352 non-electrolytic binary solutions) at 53.2° C, 74.1° C and 93.9° C. Both negative and positive deviations from Raoult's law are observed.

A portion of this data is studied through a combined Hildebrand-Scatchard and Guggenheim-Miller approach to solution theory. By regarding the solution as being "regular" and then taking into account the difference in size between the solute and solvent molecules, a modified equation is developed which quantitatively predicts (to within three percent of the measured values) the activity coefficients for a limited number of systems.

To arrive at a more general formulation, the mathematical technique of factor analysis is applied to the data. This results in a method for the quantitative prediction of the activity coefficient of the solute, regardless of the size or polarity of the components of the solution. It is shown that this method can be directly applied to aid the analyst in predicting the suitability of a solvent phase for a difficult G.L.C. separation.

In conclusion, it is illustrated that the values for the experimental activity coefficients appear to be consistent with the effect of size and with the intermolecular forces (dispersion, dipole-induced dipole, dipole-dipole, hydrogen bonding, etc.) which are known to be operative in the liquid phase.